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(54) Sealant compositions

(57) The present invention relates to a sealant com-

(a) 100 parts by weight of a hydrogenated vinyl ar-  
 omatic hydrocarbon block copolymer which has an overall  
 weight average molecular weight of from 30,000 to  
 300,000, a vinyl aromatic hydrocarbon block weight

of the sealant composition according to the invention.  
 solution containing a solvent and at least 30 % by weight  
 of the sealant to a sealant

ing resin.

(b) 20-400 parts by weight of an adhesion promot-  
 ing resin.  
 And wherein the butadiene block has a vinyl content  
 of at least 45% by weight, and  
 average molecular weight of from 4000 to 35,000,

(57) The present invention relates to a sealant com-

(54) Sealant compositions

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Anionic polymerization of conjugated diene hydrocarbons with lithium initiators is well known as described in U.S. Patents Nos. 4,039,593 and RE. 27,145 which describes an initiator which builds a living polymer backbone at each lithium menes with a monolithium, dilithium, or poly(lithium imide) initiator by reference. Polymerization com-

The biaxidene used herein must produce a polymer block with a high vinyl content. In other words, the percent of 1,2-addition of the biaxidene should be at least 45%wt, preferably 45 to 90%wt. Below 45%wt, polymer viscosity is similar to conventional polymers and there is no advantage. Above 90%wt, the viscosity decrease has reached a plateau and no longer drops with higher 1,2 content. Therefore, there is no further advantage. The 1,2-vinyl content is more preferable at least 50%wt; even more preferable at least 60%wt; yet even more preferable at least 70%wt; most preferable at least 75%wt. The 1,2-vinyl content is more preferable at most 85%wt, even more preferable at most 80%wt.

The endblocks of the block copolymers to be used in the sealant composition according to the invention are butadiene, and Y is a coupling agent.

where A is a polymer block of a vinyl aromatic hydrocarbon, preferably styrene, B is a polymer block of hydrogenated

$$(A-B)^x - y$$

This invention provides sealant compositions which comprises a hydrogenated vinyl aromatic hydrocarbon-butadiene-vinyl aromatic hydrocarbon (SEBS) block copolymer which has an overall weight average molecular weight of from 30,000 to 300,000, a vinyl aromatic hydrocarbon block copolymer which has an overall weight average molecular weight of at least 45% by weight (%wt), preferably 45 to 90%, and a sealant composition may further comprise tackifying resins. For every 100 parts by weight of block copolymer, there should be 20-400, and preferably 60 to 350 parts by weight of adhesion-promoting resin. Optionally, the sealant composition may further comprise polyvinyl alcohol hydrocarbon resins, flow promoting resins, low temperature resins, oils, polyolefins, fillers, waxes, and/or solvents.

There are at least two major criteria in formulating a sealant composition. The sealant must possess some degree of slump resistance at high service temperatures. Additionally, the sealant should have a good working viscosity in the melt so it can be easily coated on to various substrates, and/or the sealant should have a low solution viscosity in solutions containing a high amount ( $\geq 30\text{ wt\%}$ , preferably  $\geq 40\text{ wt\%}$ ) of solids.

This invention relates to sealant compositions for use as insulation against air and moisture, sound-deadening, and other functions in construction, automotive, and consumer applications. More particularly, this invention relates to such compositions containing new vinyl content hydrogenated vinyl aromatic hydrocarbon-butadiene-vinyl aromatic hydrocarbon (SEBS) block copolymers.

### Description

The hydrogenation of these polymers may be carried out by a variety of well established processes including hydrogenation metal catalysts as Raney Nickel, noble metals such as platinum, and palladium and soluble transition metal catalysts. Suitable hydrogenation processes which can be used are ones wherein the diene-containing polymer or copolymer is dissolved in an inert hydrocarbon diluent such as cyclohexane and hydrogenated by reaction with hydrogen in the presence of a soluble hydrogenation catalyst. Such processes are disclosed in U.S. Patent Nos. 3,113,986, 4,226,952 and Reissue 27,145, the disclosures of which are herein incorporated by reference.

wherein R is an aliphatic, cycloaliphatic, alkyl-substituted cycloaliphatic, aromatic or alkyl-substituted aromatic hydrocarbon radicals having from 1 to 20 carbon atoms.

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The anionic polymerization of the conjugated diene hydrocarbons is typically controlled with structure modifiers such as dicyliophenyl gylme (1,2-dithioxoethane) to obtain the desired amount of 1,2-addition. As described in part 27 145 which is incorporated by reference herein, the level of 1,2-addition of a butadiene polymer or copolymer can radically affect its cosmetic properties after hydrogellation. The 1,2-addition of butadiene polymers significantly and surprisingly additionally influences the polymer as described above. A 1,2-addition of about 40% is achieved during polymerization at 50°C with about 6% by volume of diethyl ether or about 200 ppm of ethyl glyme in the final solution. 1,2-addition of about 47% (within the scope of this invention) is achieved during polymerization at 50°C with about 300 ppm of 1,2-dithioxoethane (ODMB) in the final solution. A 1,2-addition of about 78% (within the scope of this invention) is achieved during polymerization by the presence of 1,2-dithioxopropane (DEP) in the final solution.

wherein B represents polymerized units of one or more conjugated diene hydrocarbons such as butadiene or isoprene, C represents polymerized units of one or more vinyl aromatic hydrocarbons such as styrene, X is the residue of a monoaluminum initiator such as sec-butyllithium, and Y is the residue of a dilithium initiator such as the diladduct of sec-butyllithium and m-diisopropenylbenzene. Some structures, including those preparing to poly lithium initiators of and conjugated diene and a conjugated diene, generally have limited practical utility although known in the art.

L-A-B-Y-B-A-L

17-B-Y-B-17

X-A-B-A-U

A-A-B-G

EP 0 863 193 A1

A composition of polymeric polymer and a specific polymeric polymer having a specific composition, which is obtained by polymerization of a specific monomer, and a specific composition of a specific polymer.

Other adhesion promoting resins which are also useful in the compositions of this invention include hydrogenated rosins, esters of rosins, polyesters, terephenephenol resins and polymerized olefins; lower softening point resins and liquid resins. An example of a liquid resin is Adaptic LV resin from Hercules. To obtain good thermooxidative and color stability, it is preferred that the tackifying resin be a saturated resin, e.g., a hydrogenated dicyclopentadiene resin such as Escorze® 500 series resin made by Exxon or a hydrogenated polystyrene or polyalphamethylstyrene resin such as Escorze® 5000 series resin made by Hercules. Ring and ball softening points of solid resins may be from 40°C to 140°C, preferably 80 to 115°C, as determined by ASTM E28. Liquid resins, i.e., softening points less than room temperature, may be used as well as combinations of solid and liquid resins. The selection of the particular tackifying agent is, in large part, dependent upon the specific polymer employed in the adhesive sealant composition.

A common tackifying resin is a diene-olefin copolymer of piperylene and 2-methyl-2-butene having a softening point of about 95°C. This resin is available commercially under the trade name Winalack® 95 and is prepared by the cationic polymerization of 60% piperylene, 10% isoprene, 5% cyclo-pentadiene, 15% 2-methyl-2-butene and about 10% dimer, as taught in U.S. Patent No. 3,577,398. Other tackifying resins may be employed wherein the resinsous copolymer comprises 20-80 weight percent of piperylene and 80-20 weight percent of 2-methyl-2-butene.

In sealant applications, it is common practice to add an adhesive resin such as a tackifying resin that is compatible with the polymer, generally from 20 to 400 parts per hundred parts of polymer by weight (pbw). Preferably 60 to 350 pbw. For every 100 parts by weight (pbw) of copolymer, there should be at least 20 pbw of resin to achieve the low viscosity and economics required for sealant applications. No more than 400 pbw adhesion promoting resin per 100 parts polymer can be used or the sealant will not have the visco-elastic properties required to resist flow after application.

The poly(vinyl aromatic hydrocarbon) content, typically the polystyrene content, is preferably in the range from 15 to 45 % by weight on the basis of the total polymer, more preferably from 20 to 40 %wt, even more preferably from 25 to 35 %wt.

The hydrogenated vinyl aromatic hydrocarbon-*butadiene-vinyl aromatic hydrocarbon-bis*-butadiene has an overall weight average molecular weight of from 45,000 to 200,000. The vinyl aromatic hydrocarbon polymer preferably has an average molecular weight of from 5,000 to 32,000.

2. Light Scattering from Polymer Solution. M. B. Huglin, ed., Academic Press, New York, NY, 1979.
3. W. Kaye and A. J. Hawlik, *Aplied Optics*, 12, 541 (1973).
4. M. L. McConnell, *American Laboratory*, 63, May, 1978.

Measurement of the true molecular weight of the final coupled radial or star polymer is not as straightforward as easy to make using GPC. This is because the radial or star shaped molecules do not separate and elute through the packed GPC columns in the same manner as do the linear polymers used for the calibration, and, hence, the time of arrival at a UV or refractive index detector is not a good indicator of the molecular weight. A good method to use for a radial or star polymer is to measure the weight average molecular weight by light scattering techniques. The sample is dissolved in a suitable solvent at a concentration less than 0.5 microns pore size directly into the light scattering cell. The light scattering measurements are performed as a function of scattering angle and of polymer concentration using standard procedures. The differential refractive index (DRI) of the sample is measured at the same wavelength and in the same solvent used for the light scattering. The following references relate to the subject of measuring molecular weight.

The molecular weights of linear polymers or unsarable segments of star polymers such as mono-, di-, triblock, etc., or the arms of GPC systems before coupling are conveniently measured by Gel Permeation Chromatography (GPC), where the GPC system has been appropiatly calibrated, typically with polystyrene standards of known molecular weight. For unioinically polymerized linear polymers, the polymer is essentially monodisperse (weight average molecular weight/number average molecular weight ratio) with polydispersity indices (PDIs) of known magnitude to report the "peak" molecular weight of the narrow molecular weight distribution observed. Usually, the peak value is between the number and the weight average. The peak molecular weight is the weight of the main species shown on the chromatograph. For polydisperse polymers the weight average molecular weight should be calculated from the chromatograph. The peak molecular weight is the molecular weight of the benzene gels or silica gels. The solvent is tetrahydrofuran and the detector is a refractive index detector.

fillers for constructions which will be baked (for example, in a paint baking oven) after the sealant is applied. This would sealant compositions of this invention can be used for many applications. Particularly preferred is their use as gap fillers for constructions which will be baked (for example, in a paint baking oven) after the sealant is applied. This would

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sealant compositions may then be used in a wide variety of applications. Alternatively, the ingredients may be blended into a solvent.

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The resultant compositions of blending are known to the art and any method that produces a homogeneous blend is satisfactory. Various methods of blending are known to the art and any method that produces a homogeneous blend is satisfactory. Preferredly between 50°C and 200°C, until a homogeneous blend is obtained, usually less than three (3) hours. Sealant compositions of the present invention can be prepared by blending the components at an elevated temperature, preferably between 50°C and 200°C, until a homogeneous blend is obtained, usually less than three (3)

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. The sealant compositions of the present invention can be prepared by blending the components at an elevated

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having properties suitable for many different applications.

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A formulator skilled in the art will see tremendous versatility in the polymers of this invention to prepare sealants

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containing is as low as possible to minimize shrinkage.

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pigment will be selected to give appropriate durability and color. Since sealants are applied in fairly thick layers, solvent

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usually used. Resins and plasticizers will be selected to maintain low modulus and minimize dirt pick-up. Fillers and

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of whitishandling this movement. Since sealants are frequently exposed to the weather, the hydrogenerated polymers are

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Since the two substrates frequently move relative to each other, sealants are usually low modulus compositions capable

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Sealants are gap fillers. Therefore, they are used in fairly thick layers to fill the space between two substrates.

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Sealants are gap fillers. Thereafter, they are used in fairly thick layers to fill the space between two substrates.

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Having properties needed in the composition for any specific adhesive, coating or sealant application.

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All sealant compositions based on the polymers of this invention will contain some combination of the various

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stabilizers should be compatible with the essential stabilizers mentioned hereinabove and their intended function as

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during the life of the article against, for example, ozone and ultra-violet radiation. However, these additional

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additonal stabilizers known in the art may also be incorporated into the composition. These may be for protection

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against ultraviolet radiation (organox® 1010 with bis(2,4-di-t-butyl)pentamethyl diphenophite (Uiranox® 626 from Borg-Warner).

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Phenyl(propionate)-methane (organox® 1010 from Ciba-Geigy) with triis(nonylphenyl)-phosphite (Polygard® HR from Uniroyal), organox® 1010 with bis(2,4-di-t-butyl)pentamethyl diphenophite (Uiranox® 626 from Borg-Warner).

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Combination of primary and secondary antioxidants are preferred. Such combinations include sterically hindered phenolics with phosphites or thioethers, such as hydroxyphenylpropionates with aryl phosphites or thioethers, or amino

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phenolics with phosphites or thioethers, such as hydroxyphenylpropionates with aryl phosphites or thioethers, or amino

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phenolics with phosphites or thioethers, such as hydroxyphenylpropionates with aryl phosphites or thioethers, or amino

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phenolics with phosphites or thioethers, such as hydroxyphenylpropionates with aryl phosphites or thioethers, or amino

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phenolics with phosphites or thioethers, such as hydroxyphenylpropionates with aryl phosphites or thioethers, or amino

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phenolics with phosphites or thioethers, such as hydroxyphenylpropionates with aryl phosphites or thioethers, or amino

Temperature dependent properties, such as shear adhesion failure temperature (SAFT) and slump temperature, were measured. A Brookfield Viscometer model RVT-D and spindle 29 was used to measure the viscosity at 177°C. To measure the slump temperature, the sealant formulation was poured hot and allowed to solidify in metal channels with the following dimensions: 2.5cm wide, by 2.5cm high, and 1.25cm deep. The channels were placed vertically in an oven and the temperature was raised in 5°C increments, allowing the sample to equilibrate for 30 minutes at each temperature before increasing the temperature again. The slump temperature was determined at which the sample sagged more than 3/16 inch in the channel. SAFT was determined on a lap-shear bond of 2.5cm x 2.5cm area on an aluminum surface under a load of 190g. The temperature was ramped up from 40°C in 5°C increments over 10 minutes until bond failure occurred.

## Sealant Results

Sealant Results				
Polymer	Sealant Viscosity at 177° (350°F) (CP)	Shear Adhesion Failure Temperature (°C)	Silmp Temperature (°C)	
A	33,500	73	105	
PP-5828	1,190	54.5	80	
B	5,280	54.1	80	
PP-5819	1,800	52.6	60	
PP-5823	400	48.1	55	

Table 2

PP5828 is an SBRs block copolymer with a high vinyl content. Its molecular characteristics are compared with those of Polymer A, a commercial polymer whose viscosity is considered too high for most, if not all, commercial sealant applications. It can be seen that PP5828 and Polymer A are very similar except for the vinyl content: 78% of the rubber block of PP5828 is in a 1,2 microstructure compared to 38% for Polymer A. The flow properties of PP5828 are dramatically better than Polymer A as indicated by sealant viscosity (more than an order of magnitude lower). Polymer B is the block copolymer of this type that is currently used to make sealant formulations commercially. The sealant viscosity of the formulation of this invention, made with PP5828, is one fifth of that of the formulation made with Polymer B while the SFT and slump temperature are the same. Similar, PP5823 (78% 1,2 addition) exhibits much lower sealant viscosity than either Polymer A or B. PP5819 has an intermediate level of 1,2 structure (47%), but is still markedly better (lower) in sealant viscosity than Polymers A or B. The low sealant viscosity measures that the sealant composition can be mixed, pumped, and applied more easily than sealants with higher viscosity.

Table 1

Polymer Descriptions					
Polymer	MW (real)	SEBS Block Description	1,2 Bd level	PSC	
A	67,000	10-47-10	38%	29.9%	
PP-5328	56,000	10-39-10	78%	29.6%	
B	50,000	7.5-35-7.5	38%	30%	
PP-5319	38,000	6-26-6	47%	29.5%	
PP-5323	35,000	6-23-6	78%	29.3%	

Table 1

In addition to their use in automobile manufacture and in apppliance manufacture, another preferred application is their use in gasketing materials, for example, in lids for food and beverage containers. The unhydrogenated propylene may also be used in these applications.

Variations of sealant compositions that are subjects of this invention will include structural adhesives, such as contact and structural adhesives, mastics, and personal care adhesives, and laminating adhesives. Especially useful will be the low viscosity characteristic of high vinyl ethylenebutylene rubber blocks for ease of adhesive application, e.g., sprayability.

composition as claimed in any one of the preceding claims.

- Sealant solutions containing a solvent and at least 30 % by weight on the basis of the total solution of a sealant

Seaboard composition according to any one of the preceding claims, further comprising a reinforcing resin.

b. Serialant composition according to any one of the preceding claims, further comprising a plasticizer.

Seafarant composition according to any one of the preceding claims further comprising a filler.

4. Saturated composition according to any one of claims 1-3 wherein the vinyl aromatic hydrocarbon block molecular weight is from 5,000 to 32,000.

sedatin composition according to claim 1 or 2 wherein the overall weight average molecular weights is from 45,000 to 200,000.

Sealant composition according to claim 1 wherein the vinyl content is from 45 to 90% by weight.

(a) 100 parts by weight of a hydrogenated vinyl aromatic hydrocarbon butadiene-vinyl aromatic hydrocarbon block copolymer which has an overall weight average molecular weight of from 30,000 to 300,000, a vinyl aromatic hydrocarbon block having at least 45% by weight diene block has a vinyl content of at least 45% by weight, and (b) 20-400 parts by weight of an adhesive promoting resin.

#### 1. Sealant composition which comprises:

## Claims

Quidna 68 is a hydrogenerated paraffinic processing oil (plasticiser). Kresillex F100 is an aromatic remnrocinc resin. Regalite R101 is a hydrogenerated hydrocarbon tackifying resin.

Sealant formulation	1	2	A
PP 5828	160 g	-	
Regalite R 101	-	16.0 g	
Ondina 68	44.0 g	9.6 g	
n-butyl acetate	10.4 g	10.4 g	
Toluene	80.0 g	80.0 g	
	46.0 g	40.0 g	

Table 3

Block copolymers PP 5B28 and B described in Example 1 were used to prepare sealant formulation solutions containing 40 % by weight of solids as shown in table 3. The solution viscosity was determined at 25°C using a Brookfield viscometer. The sealant formulation containing polymer B (not according to the invention) had a solution viscosity of 89.2 centipoise, whereas the sealant formulation containing polymer PP 5B28 according to the invention had a solution viscosity of 22.8 centipoise. A low solution viscosity at 40 % solids content is advantageous as the sealant can then be easily applied, or alternatively, the solids content can then be increased to e.g. 50-90 % by weight, preferably 65 to 85% by weight.

### Example 2

DOCUMENTS CONSIDERED TO BE RELEVANT												
Category	Citation of document with indication, where applicable, of relevant passages	Relevant to claim	CLASSIFICATION (Int'l Cls.) APPLICATON OF THE									
A	WO 95 12645 A (SHELL INT RESEARCH) 11 May 1995 * page 10, line 26 - page 14, line 16 *	1-8 C09K3/10 C08L53/02	US 4 242 245 A (ALLISON GEORGE M III) 30 December 1980 * the whole document *									
A	EP 0 322 055 A (SHELL INT RESEARCH) 28 June 1989 * the whole document *	1-8 I-8	FR 2 423 460 A (BOSTIK SA) 16 November 1979 * Page 5, line 11 - page 9, line 18 *									
A	EP 0 367 165 A (HERCULES INC) 9 May 1990 * claims *	I-8 I-8	EP 0 822 227 A (SHELL INT RESEARCH) 4 February 1998 * the whole document *									
P,A	EP 0 822 227 A (SHELL INT RESEARCH) 4 February 1998 * claims; table I *	I I-8										
<p>The present search report has been drawn up for all claims</p> <table border="1"> <tr> <td>THE HAGUE</td> <td>II June 1998</td> <td>Puttz, C</td> </tr> <tr> <td colspan="2">Date of completion of the action</td> <td>Examiner</td> </tr> <tr> <td colspan="3">Place of search</td> </tr> </table>				THE HAGUE	II June 1998	Puttz, C	Date of completion of the action		Examiner	Place of search		
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<p>CATEGORY OF CITED DOCUMENTS</p> <p>T: Treaty or complete analogy the invention X: Patentability relevant to action alone Y: Patentability relevant if combined with another Z: Document cited in the application A: Document cited for other reasons B: Document cited in the application C: Document cited for other reasons D: Document cited in the application E: earlier patent document, but published on, or F: International document G: Non-patent document H: Document of the same category I: Member of the same family, corresponding document</p>												

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Application Number

### EUROPEAN SEARCH REPORT

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European Patent

